

## 2. ALGORITHM OVERVIEW

In this chapter, algorithms that generally apply across a range of compartment types are discussed. Algorithms specific to compartment types are presented in subsequent chapters.

### 2.1 MULTIPLE-PHASE CALCULATIONS

This section describes how multiple phases within a compartment are currently modeled. The most common phases considered in the prototype are liquid, gas, and solid, which are assumed to be at chemical equilibrium. Other phases may include biotic phases (*e.g.*, algae in surface water). Because chemical equilibrium among phases in a compartment is assumed, the ratios of the concentrations in the individual phases are constant, and mass balance need only be tracked for the total amount of the chemical in all phases in a compartment. The amount of chemical in the compartment in a particular phase can be determined from the total amount in the compartment (described in the following text). It is possible that, in future versions of TRIM.FaTE, chemical equilibrium will not be assumed, in which case the amount of chemical in different phases will need to be tracked as separate compartments.

In any compartment, the total amount of chemical in a given compartment is made up of the sum of the amounts in the different phases:

$$N^{Total} = \text{Amount in gas phase} + \text{Amount in aqueous phase} + \text{Amount in solid phase} \quad (2-1)$$

$$= C^{gas}V^{gas} + C^{water}V^{water} + C^{solid}V^{solid}$$

where:

$N^{Total}$	=	total amount of chemical in compartment (g [chemical])
$C^{gas}$	=	concentration of chemical in gas phase in compartment (g [chemical]/m <sup>3</sup> [gas in compartment])
$V^{gas}$	=	volume of gas in compartment (m <sup>3</sup> [gas in compartment])
$C^{water}$	=	concentration of chemical in aqueous phase in compartment (g [chemical]/m <sup>3</sup> [water in compartment])
$V^{water}$	=	volume of aqueous matter in compartment (m <sup>3</sup> [water in compartment])
$C^{solid}$	=	concentration of chemical in solid phase in compartment (g [chemical]/m <sup>3</sup> [solid in compartment])
$V^{solid}$	=	volume of solid in compartment (m <sup>3</sup> [solid in compartment]).

If it is desired that the units of  $N^{Total}$  be in units of moles (chemical), then the preceding equation must be multiplied by the molecular weight of the chemical (which has units of moles [chemical]/g [chemical]).

Because chemical equilibrium is assumed, the ratios of the concentrations are constant. However, care must be used in specifying the units of the concentration. This is because, in

practice, it is more common to define notation for ratios of concentrations on a mass by mass basis rather than that of mass by volume basis.

### 2.1.1 NORMALIZATION TO LIQUID PHASE

This section describes the relevant formulas when the concentrations in other phases are normalized to the concentration in the liquid phase. This normalization is used for all soil, surface water, and sediment compartments (including the cases where additional phases are considered). Using the equilibrium assumptions:

$$C^{solid} = (\rho_{solid} K_d C_f) C^{water} \quad (2-2)$$

$$C^{gas} = (H/RT) C^{water} \quad (2-3)$$

where:

$\rho_{solid}$	=	density of solid phase in compartment (kg [solid phase]/m <sup>3</sup> [solid phase])
$K_d$	=	equilibrium partition coefficient; ratio of concentration in solid phase (kg [chemical]/kg [solid phase]) to that in liquid phase (kg [chemical]/liters [L][liquid phase])
$C_f$	=	10 <sup>-3</sup> m <sup>3</sup> /L, conversion factor to convert m <sup>3</sup> (liquid phase) to L (liquid phase)
$H$	=	Henry's law constant for chemical (Pa-m <sup>3</sup> /mol)
$R$	=	ideal gas constant (8.314 m <sup>3</sup> -Pa/mol-K)
$T$	=	temperature (K)

Applying these relationships to the general equation in the beginning of this section yields:

$$N^{Total} = C^{water} \left( \frac{H}{RT} V^{gas} + V^{water} + \rho_{solid} K_d C_f V^{solid} \right) \quad (2-4)$$

The volumes of each phase in the compartment can be expressed as fractions of the total volume of the compartment, in which case the previous equation yields:

$$N^{Total} = C^{water} V^{Total} \left( \frac{H}{RT} \frac{V^{gas}}{V^{Total}} + \frac{V^{water}}{V^{Total}} + \rho_{solid} K_d C_f \frac{V^{solid}}{V^{Total}} \right) \quad (2-5)$$

where:

$$V^{Total} = V^{gas} + V^{water} + V^{solid}$$

The term  $C^{Total} = N^{Total}/V^{Total}$  is the total concentration of the chemical in the compartment. Using the assumed equilibrium relationships, the concentrations in the individual phases can be recovered from the total amount of mass in the compartment, as follows:

$$C^{water} = \frac{N^{Total}/V^{Total}}{\left( \frac{H}{RT} \frac{V^{gas}}{V^{Total}} + \frac{V^{water}}{V^{Total}} + \rho_{solid} K_d C_f \frac{V^{solid}}{V^{Total}} \right)} \quad (2-6)$$

$$C^{gas} = \frac{H}{RT} C^{water} = \frac{(H/RT) N^{Total}/V^{Total}}{\left( \frac{H}{RT} \frac{V^{gas}}{V^{Total}} + \frac{V^{water}}{V^{Total}} + \rho_{solid} K_d C_f \frac{V^{solid}}{V^{Total}} \right)} \quad (2-7)$$

$$C^{solid} = \rho_{solid} K_d C_f C^{water} = \frac{(\rho_{solid} K_d C_f) N^{Total}/V^{Total}}{\left( \frac{H}{RT} \frac{V^{gas}}{V^{Total}} + \frac{V^{water}}{V^{Total}} + \rho_{solid} K_d C_f \frac{V^{solid}}{V^{Total}} \right)} \quad (2-8)$$

For cases in which the concentration in the water phase is negligible (*e.g.*, when compartment is air, or the chemical has a very low solubility), the concentrations must be normalized to another phase.

## 2.1.2 FRACTION OF CHEMICAL IN EACH PHASE WHEN PHASES ARE IN EQUILIBRIUM

### 2.1.2.1 General Form

If a chemical is in equilibrium among several phases within a compartment, it is straightforward to calculate the fraction of the chemical that is in each phase. In particular, if there are  $n$  phases in equilibrium, with:

$$\begin{aligned} C_1 &= \kappa_1 C_{norm} \\ C_2 &= \kappa_2 C_{norm} \\ C_3 &= \kappa_3 C_{norm} \\ &\vdots \\ C_n &= \kappa_n C_{norm} \end{aligned} \quad (2-9)$$

where  $C_j$  is the concentration of the chemical in phase  $j$  (units of mass [chemical]/volume [phase  $j$ ]),  $C_{norm}$  is the concentration in the phase to which one is normalizing, and  $\kappa_j$  is the equilibrium ratio between the concentration in phase  $j$  and the phase to which one is normalizing, with units of (mass [chemical]/volume [phase  $j$ ])/(mass [chemical]/volume [phase to which one is normalizing]). These ratios  $\kappa_j$  are generally expressed in terms of other environmental and/or chemical parameters. The total mass of chemical in the compartment, denoted by  $N^{Total}$ , is:

$$\begin{aligned} N^{Total} &= \sum_{j=1}^n V_j C_j \\ &= \sum_{j=1}^n V_j \kappa_j C_{norm} \\ &= C_{norm} \sum_{j=1}^n V_j \kappa_j \end{aligned} \quad (2-10)$$

where  $V_j$  is the volume of phase  $j$  in the compartment, and  $\sum_{j=1}^n V_j = V_{total}$ . The fraction of mass of chemical in phase  $j$  is then given by:

$$\begin{aligned} \frac{\text{Mass of chemical in phase } j \text{ in compartment}}{\text{Total mass of chemical in compartment}} &= \frac{V_j C_j}{N^{Total}} \\ &= \frac{V_j \kappa_j C_{norm}}{C_{norm} \sum_{j'=1}^n V_{j'} \kappa_{j'}} \\ &= \frac{V_j \kappa_j}{\sum_{j'=1}^n V_{j'} \kappa_{j'}} \end{aligned} \quad (2-11)$$

When applied to the previous section (and using the notation introduced there), we have that  $C_{norm} = C_{water}$  and the terms  $\kappa$  are given by:

$$\kappa_{water} = 1 \quad (2-12)$$

$$\kappa_{gas} = H/(RT) \quad (2-13)$$

$$\kappa_{solid} = \rho_{solid} K_d C_f \quad (2-14)$$

### 2.1.2.2 Form When Fugacity Concept Is Applicable

It is sometimes convenient to apply the concept of fugacity (Mackay 1991) when presenting the equations. For the chemicals modeled to date (PAH, B(a)P, elemental mercury, divalent mercury, and methylmercury), the algorithms are presented using the fugacity notation. Fugacity has units of pressure and can be linearly or non-linearly related to concentration through the relationship fugacity ( $f$ ) = (fugacity capacity [ $Z$ ]) · (concentrations). The fugacity capacities for the pure phases of water, air, and solid are:

$$Z_{water} = 1/H \quad (2-15)$$

$$Z_{air} = 1/(RT) \quad (2-16)$$

$$Z_{solid} = \rho_{solid} K_d C_f Z_{water} \quad (2-17)$$

defined by:

$\rho_{solid}$	=	density of solid phase in compartment (kg [solid phase]/m <sup>3</sup> [solid phase])
$K_d$	=	equilibrium partition coefficient; ratio of concentration in solid phase (kg [chemical]/kg [solid phase]) to that in liquid phase (kg [chemical]/liters [L][liquid phase])
$C_f$	=	10 <sup>-3</sup> m <sup>3</sup> /L, conversion factor to convert m <sup>3</sup> (liquid phase) to L (liquid phase)
$H$	=	Henry's law constant for chemical (Pa-m <sup>3</sup> /mol)
$R$	=	ideal gas constant (8.314 m <sup>3</sup> -Pa/mol-K)
$T$	=	temperature (K)

The total fugacity capacity  $Z^{Total}$  for a given compartment is defined as:

$$Z^{Total} = Z_{air} \frac{V^{gas}}{V^{Total}} + Z_{water} \frac{V^{water}}{V^{Total}} + Z_{solid} \frac{V^{solid}}{V^{Total}} \quad (2-18)$$

where phase is either the solid, liquid, gas, or other phase.

It is fundamental to the concept of partition modeling that the concentration ratio between two phases is equal to the ratios of the fugacity capacities of the two phases (Mackay 1991). That is,

$$\frac{C^{phase_1}}{C^{phase_2}} = \frac{Z_{phase_1}}{Z_{phase_2}} \quad (2-19)$$

Applying these relationships shows that:

$$C^{water} = \frac{Z_{water}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = \frac{Z_{water}}{Z^{total}} C^{total} \quad (2-20)$$

$$C^{gas} = \frac{Z_{air}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = \frac{Z_{gas}}{Z^{total}} C^{total} \quad (2-21)$$

$$C^{solid} = \frac{Z_{solid}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = \frac{Z_{solid}}{Z^{total}} C^{total} \quad (2-22)$$

where  $C^{Total}$  is the total concentration of the chemical in the compartment (units of g [chemical]/m<sup>3</sup>[total compartment]). From these relationships, in general, the amount of mass in the different phases is given by:

$$N^{water} = V^{water} C^{water} = V^{water} \frac{Z_{water}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = V^{water} \frac{Z_{water}}{Z^{total}} C^{total} \quad (2-23)$$

$$N^{gas} = C^{gas} V^{gas} = V^{gas} \frac{Z_{air}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = V^{gas} \frac{Z_{gas}}{Z^{total}} C^{total} \quad (2-24)$$

$$N^{solid} = C^{solid} V^{solid} = V^{solid} \frac{Z_{solid}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = V^{solid} \frac{Z_{solid}}{Z^{total}} C^{total} \quad (2-25)$$

where  $N^{water}$ ,  $N^{gas}$ , and  $N^{solid}$  are the mass in the water, gas, and solid phases, respectively.

If there are other phases in equilibrium with the chemical dissolved in the water phase, then the fugacity capacities of that phase can be defined in a manner consistent with that above. For example, if  $C_{other} = \kappa_{other} C_{water}$ , where  $C_{other}$  has units of g[chemical]/m<sup>3</sup>[other phase], then the fugacity capacity of the other phase is defined by:

$$Z_{other} = \kappa_{other} Z_{water} \quad (2-26)$$

and the total fugacity capacity of the compartment is given by:

$$Z^{Total} = Z_{air} \frac{V^{gas}}{V^{Total}} + Z_{water} \frac{V^{water}}{V^{Total}} + Z_{solid} \frac{V^{solid}}{V^{Total}} + Z_{other} \frac{V^{other}}{V^{Total}} \quad (2-27)$$

where  $V^{other}$  is the volume of the other phase, in units of m<sup>3</sup>[other phase].

In the following sections, the general equations presented in this section for multiple phase calculations are applied to specific compartment types. The use of these equations in the

following sections primarily involves only adhering to notation commonly used in the literature for the different media.

### 2.1.3 APPLICATION TO SOIL, SURFACE WATER, AND SEDIMENT COMPARTMENT TYPES

For soil, surface water, and sediment compartment types, the concentrations are normalized to the concentration in the liquid phase, and the same notation is used to represent the relevant parameters. In a soil compartment, the solid phase consists of the soil particles. In a surface water compartment, the solid phase consists of the sediment suspended in the water column. In a sediment compartment, the solid phase consists of clay, silt, or sand particles as opposed to the water phase that fills the interstitial space between the sediment solid particles. Following common practice, the volume fractions of each phase are denoted as follows:

$$\frac{V^{water}}{V^{total}} = \theta \quad (2-28)$$

$$\frac{V^{gas}}{V^{total}} = \epsilon \quad (2-29)$$

$$\frac{V^{solid}}{V^{total}} = 1 - \theta - \epsilon = 1 - \phi \quad (2-30)$$

where:

$$\begin{aligned} \theta &= \text{water volume fraction} \\ \epsilon &= \text{gas volume fraction} \\ 1 - \theta - \epsilon &= 1 - \phi = \text{solid volume fraction} \end{aligned}$$

where  $\phi$  is the total porosity of the compartment ( $= \theta + \epsilon$ ). The equations for the total mass of chemical in the compartment and in the different phases are then given by:

$$N^{Total} = C^{water} V^{Total} \left( \frac{H}{RT} \epsilon + \theta + \rho_{solid} K_d C_f (1 - \phi) \right) \quad (2-31)$$

If there are other phases in equilibrium with the chemical in the water phase, then the previous equation is augmented as follows:

$$N^{Total} = C^{water} V^{Total} \left( \frac{H}{RT} \epsilon + \theta + \rho_{solid} K_d C_f \left( 1 - \phi - \sum_{j=1}^m \psi_j \right) + \sum_{j=1}^m K_j \psi_j \right) \quad (2-32)$$

where:

$$\begin{aligned}
 K_j &= \text{equilibrium ratio of concentration of chemical in phase } j \text{ and concentration} \\
 &\quad \text{dissolved in water phase (g [chemical]/m}^3 \text{ [phase } j\text{])}/(\text{g [chemical]}/\text{m}^3 \\
 &\quad \text{[water]}) \\
 \psi_j &= \text{volume fraction of compartment composed of phase } j \text{ (} \\
 &\quad \text{m}^3 \text{[phase } j\text{]}/\text{m}^3 \text{[total]})
 \end{aligned}$$

### ***Fugacity-based Notation***

If fugacity-based notation is to be used, then the total fugacity for the compartment is given by:

$$Z^{total} = Z_{air} \epsilon + Z_{water} \theta + Z_{solid} (1 - \phi) \quad (2-33)$$

In the general case when there are additional equilibrium phases considered:

$$Z^{total} = Z_{air} \epsilon + Z_{water} \theta + Z_{solid} \left( 1 - \phi - \sum_{j=1}^m \psi_j \right) + \sum_{j=1}^m Z_j \psi_j \quad (2-34)$$

where  $Z_j$  is the fugacity of phase  $j$ .

Note that for the ground water, surface water, and sediment compartment types, the volume fractions of the gas phase ( $\epsilon$ ) are assumed to be zero.

The soil-water partition coefficients ( $K_d$ ) in each compartment (soil, surface water, and sediment) may be either input or calculated. At present, they are input for mercury species, and calculated for nonionic organic chemicals (Karickhoff 1981) by:

$$K_d = K_{oc} f_{oc} \quad (2-35)$$

where:

$$\begin{aligned}
 K_{oc} &= \text{organic-carbon partition coefficient} \\
 f_{oc} &= \text{fraction of organic carbon in the compartment.}
 \end{aligned}$$

## **2.1.4 MULTIPHASE PARTITIONING IN THE AIR COMPARTMENT TYPE**

Because the volume of water in an air compartment is so small relative to the volume of the solid and the gas phase, there has not been a historical development of  $K_d$ 's (*i.e.*, ratio of concentration in solid phase to that in dissolved phase) for the atmosphere, although the concept still applies. Instead, only the solid and gas phases are usually addressed. If chemical equilibrium is assumed between the phases, then a normalization other than to the liquid



concentration is required. In an air compartment, the solid phase consists of the particulate matter in the atmosphere.

At present, the volume fractions of solids in each phase in an air compartment are given by:

$$\frac{V^{water}}{V^{total}} = 0 \quad (2-36)$$

$$\frac{V^{solid}}{V^{total}} = D_L / \rho_{dust} \quad (2-37)$$

$$\frac{V^{gas}}{V^{total}} = 1 - D_L / \rho_{dust} \quad (2-38)$$

where:

$$\begin{aligned} D_L &= \text{atmospheric dust load in air compartment (kg [aerosol]/m}^3 \text{ [air compartment])} \\ \rho_{dust} &= \text{density of aerosols (kg [aerosol]/m}^3 \text{ [aerosol])}. \end{aligned}$$

The dust load and aerosol density are specified properties of each air compartment. To normalize to either the gas or solid phase, the equilibrium ratio of the concentrations in the two phases must be estimated. In the prototype, the fraction of the contaminant bound to particles, denoted by  $\phi$ , is estimated using a method developed in Junge (1977) for organics, and a more recent method developed by Harner and Bidleman (1998) that is applied for mercury, both of which are discussed in the subsequent sections. Use of this term in the current notation is:

$$V^{solid} C^{solid} = \phi \quad (2-39)$$

$$V^{gas} C^{gas} = 1 - \phi \quad (2-40)$$

From this, the equilibrium ratio of the concentration in the solid phase to that in the gas phase in an air compartment is given by:

$$\begin{aligned} \frac{C^{solid}}{C^{gas}} &= \frac{\phi / V^{solid}}{(1 - \phi) / V^{gas}} \\ &= \frac{\phi / (D_L / \rho_{dust})}{(1 - \phi) / (1 - D_L / \rho_{dust})} \\ &= \frac{\phi (1 - D_L / \rho_{dust})}{(1 - \phi) (D_L / \rho_{dust})} \end{aligned} \quad (2-41)$$

The total mass of chemical in the air compartment is then:

$$\begin{aligned}
 N^{Total} &= C^{gas} V^{Total} \left( (1 - DL/\rho_{dust}) + \frac{C^{solid}}{C^{gas}} (DL/\rho_{dust}) \right) \\
 &= C^{gas} V^{Total} \left( (1 - DL/\rho_{dust}) + \frac{\phi(1 - DL/\rho_{dust})}{(1 - \phi)(DL/\rho_{dust})} (DL/\rho_{dust}) \right) \\
 &= C^{gas} V^{Total} \left( (1 - DL/\rho_{dust}) + \frac{\phi(1 - DL/\rho_{dust})}{(1 - \phi)} \right) \\
 &= C^{gas} V^{Total} (1 - DL/\rho_{dust}) \left( 1 + \frac{\phi}{1 - \phi} \right)
 \end{aligned} \tag{2-42}$$

### ***Fugacity-based Notation***

For the air compartment, the fugacity capacity in the solid phase can be determined by use of the relationship as follows.

$$\begin{aligned}
 Z_{solid} &= Z_{air} \frac{C^{solid}}{C^{gas}} \\
 &= Z_{air} \frac{\phi(1 - DL/\rho_{dust})}{(1 - \phi)(DL/\rho_{dust})}
 \end{aligned} \tag{2-43}$$

where  $Z_{air} = 1/(RT)$ ,  $R$  is the ideal gas constant (8.314 m<sup>3</sup>-Pa/mol-K), and  $T$  is temperature (K).

The total fugacity in the air compartment is then given by:

$$\begin{aligned}
 Z^{total} &= Z_{air} \frac{V^{gas}}{V^{Total}} + Z_{solid} \frac{V^{solid}}{V^{Total}} \\
 &= Z_{air} (1 - DL/\rho_{dust}) + Z_{solid} DL/\rho_{dust}
 \end{aligned} \tag{2-44}$$

## **2.1.5 CALCULATION OF THE FRACTION OF CONTAMINANT BOUND TO AEROSOL**

In the prototype, the fraction of chemical bound to particulate in the air compartment, denoted by  $\phi_i$ , is calculated using one of two methods. The first method discussed here is discussed in Harner and Bidleman (1998), while the second is due to Junge (1977). The current TRIM.FaTE model relies on the method of Harner and Bidleman. Note that in each of these

methods, any chemical with extremely low or essentially zero vapor pressure is assumed to be 100 percent bound to particulate matter in the air (*e.g.*, cadmium, lead).

### 2.1.5.1 $K_{OA}$ -based Method

In Harner and Bidleman (1998), a “ $K_{OA}$  absorption model” is shown to fit to PCB data better than a Junge-Pankow model similar to that discussed in the previous section. Further, the parameters needed are considered to be more easily measurable than the parameters for the Junge-Pankow model. Using the notation of that paper, this model first estimates the particle/gas partition coefficient ( $K_p$ ) in terms of the octanol-air partition coefficient and the fraction of organic matter attached to particles, and then one calculates the fraction of compound in the particle phase via the relationship:

$$\phi = \frac{K_p(TSP)}{1 + K_p(TSP)} \quad (2-45)$$

where:

$$\begin{aligned} K_p &= \text{particle/gas partition coefficient for compound} \\ &\quad (\text{ng}[\text{chemical}]/\mu\text{g}[\text{particles}]) / (\text{ng}[\text{chemical}]/\text{m}^3[\text{air}]) \\ TSP &= \text{total suspended particle concentration } (\mu\text{g}[\text{particles}]/\text{m}^3[\text{air}]) \end{aligned}$$

Using the notation of this section, the following relationship exists:

$$TSP = 10^9 D_L \quad (2-46)$$

where  $D_L$  is the dust load for the air compartment ( $\text{kg}[\text{particle}]/\text{m}^3[\text{air}]$ ).

The particle/gas partition coefficient  $K_p$  is calculated via the regression:

$$\log K_p = \log K_{OA} + \log f_{om} - 11.91 \quad (2-47)$$

where:

$$\begin{aligned} K_{OA} &= \text{octanol-air partition coefficient} \\ f_{om} &= \text{organic fraction of the aerosol} \end{aligned}$$

If the octanol-air partition coefficient is not available, it can be calculated from the octanol-water partition coefficient  $K_{ow}$  via the relationship:

$$K_{OA} = K_{OW} (RT/H) \quad (2-48)$$

where the units of  $R$ ,  $T$ , and  $H$  are such that the quantity  $RT/H$  is unitless.

### 2.1.5.2 Junge's Method

This method has been used in existing multimedia models and is available as an alternative. This discussion is based on that presented in CalTOX (McKone 1993a, McKone 1993b, McKone 1993c). With this method, the fraction of chemical bound to aerosol is calculated via the formula:

$$\phi = \frac{c \theta}{VP + c \theta} \quad (2-49)$$

where:

$VP$  = vapor pressure or subcooled vapor pressure of the chemical (Pa)  
 $c$  = empirical constant set to 0.173 as in Junge (1977) (m-Pa)  
 $\theta$  = total surface of aerosols per volume of aerosol ( $\text{m}^2/\text{m}^3$ ).

There is a range of values for  $\theta$ , with Whitby (1978) reporting a range of values of  $4.2 \times 10^{-5} \text{ m}^2/\text{m}^3$  for a “clean” continental site to  $1.1 \times 10^{-5} \text{ m}^2/\text{m}^3$  for urban sites. The average of these values is used as the default for  $\theta$ .

Following CalTOX (McKone 1993a, McKone 1993b, McKone 1993c), the subcooled vapor pressure (vapor pressure of subcooled liquid) is used if the temperature is below the melting point ( $T_m$ ) of the chemical. In particular:

$$VP = \begin{cases} VP & \text{if } T > T_m \\ \exp[6.79(T_m/T - 1)] & \text{if } T \leq T_m \end{cases} \quad (2-50)$$

where:

$VP$  = vapor pressure or subcooled vapor pressure of the chemical (Pa)  
 $T$  = temperature (K)  
 $T_m$  = melting point (K)

## 2.2 CONVERTING EQUATIONS WITH EQUILIBRIUM RELATIONSHIPS TO DYNAMIC FORM

In the course of converting equations to a form that is suitable for use within the intended framework, it is possible to convert some algorithms that represent steady-state equilibrium relationships into time-dependent ones. This can be performed if an estimate of the time required for the concentration to reach some fraction of the steady-state value is available. In particular, if the concentration in one compartment  $C_1$  is related to the concentration in another compartment  $C_2$  by an equilibrium relationship of the form  $C_1 = K C_2$ , where  $K$  is known and it is known that it

takes time  $t_\alpha$  in order to reach  $100\alpha$  percent of the steady-state value when  $C_2$  is approximately constant, then:

$$\frac{dC_1(t)}{dt} = k_2 C_2 - k_1 C_1 \quad (2-51)$$

where  $k_1$  and  $k_2$  are defined as:

$$k_1 = -\ln(1-\alpha)/t_\alpha \quad (2-52)$$

$$k_2 = K k_1 \quad (2-53)$$

The solution of the previous differential equation with initial condition  $C_1(0) = 0$  is given by:

$$C_1(t) = \frac{k_2}{k_1} C_2 (1 - e^{-k_1 t}) \quad (2-54)$$

The steady-state solution is  $C_1(t) = (k_2/k_1) C_2$ , and so  $K = k_2/k_1$ . This assumption that  $100\alpha$  percent of the steady-state value is reached at time  $t_\alpha$  means that:

$$1 - e^{-k_1 t_\alpha} = \alpha \quad (2-55)$$

Solving for  $k_1$  yields:

$$k_1 = -\ln(1-\alpha)/t_\alpha \quad (2-56)$$

When  $k_1$  is determined,  $k_2 = k_1 K$ , from which the general result (*i.e.*, Equations 2-52 and 2-53) follows.

## 2.3 GENERAL FATE AND TRANSPORT PROCESSES

### 2.3.1 ADVECTIVE PROCESSES

In general, the advective flux in a given phase (*e.g.*, attached to particles, or dissolved in water) from compartment  $i$  to compartment  $j$  is given by:

$$\text{Advective flux from compartment } i \text{ to compartment } j = (\text{Volume of phase that moves from compartment } i \text{ to compartment } j \text{ per unit time}) \times (\text{Amount of chemical in phase per volume of phase in compartment } i) \quad (2-57)$$

or

$$\begin{aligned} \text{Advective flux Compartment } i \rightarrow \text{Compartment } j &= Q(\text{phase}) \times \frac{N_i(t) \times f_i(\text{phase})}{V_i(\text{phase})} \\ &= T_{i \rightarrow j}^{\text{adv}}(\text{phase}) \times N_i(t) \end{aligned} \quad (2-58)$$

where:

$Q(\text{phase})$	=	volumetric flux of phase from compartment $i$ to compartment $j$ (m <sup>3</sup> [phase]/day)
$N_i(t)$	=	amount of chemical in compartment $i$ at time (moles [chemical])
$f_i(\text{phase})$	=	fraction of chemical in compartment $i$ that is in the moving phase (moles [chemical in phase]/moles [chemical in compartment $i$ ])
$V_i(\text{phase})$	=	volume of phase that is in compartment $i$ (m <sup>3</sup> [phase])
$T_{i \rightarrow j}^{\text{adv}}(\text{phase})$	=	phase transfer factor for advective flux from compartment $i$ to receiving compartment $j$ (1/day), given by:

$$T_{i \rightarrow j}^{\text{adv}}(\text{phase}) = \frac{Q(\text{phase}) \times f_i(\text{phase})}{V_i(\text{phase})} \quad (2-59)$$

This formula for the transfer factor is valid for all advective processes from one compartment to another, and does not rely on the fugacity concept. Application of the concept of fugacity (as presented in Section 2.1.2.2) shows that:

$$f_i(\text{phase}) = \frac{Z_i(\text{phase})}{Z_i(\text{Total})} \times \frac{V_i(\text{phase})}{V_i(\text{Total})} \quad (2-60)$$

where:

$Z_i(\text{phase})$	=	fugacity capacity for moving phase (mol/m <sup>3</sup> [phase]-Pa)
$Z_i(\text{Total})$	=	total fugacity capacity for compartment $i$ (mol/m <sup>3</sup> [sending compartment $i$ ]-Pa)
$V_i(\text{Total})$	=	total volume of compartment $i$ (sum of volumes of each phase in compartment) (m <sup>3</sup> [compartment $i$ ]).

Applying this shows that the fugacity-based form for the transfer factor for advective flux is:

$$T_{i \rightarrow j}^{adv}(phase) = \frac{Q(phase) \times Z_i(phase)}{V_i(Total) \times Z_i(Total)} \quad (2-61)$$

$$= \frac{v(phase) \times A_{ij} \times Z_i(phase)}{V_i(Total) \times Z_i(Total)}$$

In most applications, the volumetric flow rate  $Q(phase)$  of the phase is calculated as the product of a relevant area ( $A_{ij}$ ) and the volumetric flow rate per unit area, or a flow velocity ( $v_{ij}$ ). Usually the relevant area is the interfacial area between the sending and receiving compartments, but this is not always the case; *e.g.*, erosion from surface soil to surface water is usually reported in units of mass (soil)/area (soil layer)-time, in which case the relevant area is the area of the surface soil layer. Table 2-1 summarizes the velocities included for compartment types in the prototype. These flows are discussed in more detail in the sections describing the specific compartment types.

## 2.3.2 REACTION AND TRANSFORMATION PROCESSES

At present, all reaction and transformation processes are modeled using a first-order rate constant  $k$  (units of 1/day). The reaction/transformation flux within a compartment is then given by  $k N(t)$ , where  $N(t)$  is the mass of chemical in the compartment. There are a variety of ways in which the rate constant is determined, with the details depending on the compartment types and chemicals involved. The simplest is the case where the rate constant is an input (*e.g.*, for the current mercury species transformation algorithms). In other cases, the rate constant may be calculated from other environmental and/or chemical parameters (*e.g.*, from a half-life input by the user).

## 2.3.3 BIOTIC PROCESSES

The biotic processes in TRIM.FaTE are well characterized by the descriptions of abiotic processes and conversions. Diffusive processes and advective processes are both included. The primary instance of advection is dietary uptake. Another prominent example is litterfall. Fugacity is used as a descriptor in algorithms where it is convenient (*e.g.*, in the uptake of contaminants by foliage from air). Because mechanisms of uptake of contaminants by some organisms are not well understood or are difficult to parameterize, some partitioning processes are assumed to be equilibrium relationships according to the form described in Section 2.2. These processes may be combinations of diffusion, active transport, and/or advection (*e.g.*, transport of contaminants into the plant root), and it is not necessary for the user to specify the mechanistic process, only the empirical relationship (bioconcentration factor or partition coefficient and time to equilibrium).

As with abiotic processes (Section 2.3.2), biotic transformation rates are also described as first-order processes with respect to the average chemical concentration in the particular compartment of concern.

**Table 2-1**  
**Summary of Volumetric Advective Flow Velocities Included in TRIM.FaTE Prototype V<sup>a</sup>**

Source/ Sending Compartment	Receiving Compartment	Moving Phase	Description of Advective Process	Units	Method for Calculation
Soil	Soil	Liquid	Precipitation driven percolation	m <sup>3</sup> (water)/day	$= A \cdot V_{\text{liquid}}$ where: $A$ = Area of soil-soil interface, m <sup>2</sup> $V_{\text{liquid}}$ = Darcy velocity of water in sending soil compartment, m <sup>3</sup> [water]/m <sup>2</sup> [area]-day.
		Gas	Gas discharge	m <sup>3</sup> (gas)/day	$= A \cdot V_{\text{gas}}$ where: $A$ = Area of soil-soil interface, m <sup>2</sup> $V_{\text{gas}}$ = Darcy velocity of gas in sending soil compartment, m <sup>3</sup> (gas)/m <sup>2</sup> (area)-day.
	Air	Solid	Resuspension	m <sup>3</sup> (soil)/day	It is assumed that volumetric flow of particles from soil is the same as that to soil. Volumetric resuspension rate is then  $= \text{Vol. Flow TO soil} = A \cdot v_d \cdot \rho_A / \rho_P$ where: $A$ = Area of soil-soil interface, m <sup>2</sup> (area) $v_d$ = Dry deposition velocity of particles, m/day $\rho_A$ = Atmospheric dust load in air compartment type (concentration of dust in air), kg(particles)/m <sup>3</sup> (atmosphere) $\rho_P$ = Density of air particles, kg[particles]/m <sup>3</sup> [particles]
	Surface Water	Solid	Erosion	m <sup>3</sup> (soil)/day	Calculated from mass-based areal erosion rate and soil density: $= A \cdot E / \rho_s$ where: $A$ = Area of soil layer, m <sup>2</sup> $E$ = erosion rate to surface water, kg (soil)/m <sup>2</sup> (area)-day $\rho_s$ = density of eroding soil, kg(soil)/m <sup>3</sup> (soil)



**Table 2-1 (continued)**  
**Summary of Volumetric Advective Flow Velocities Included in TRIM.FaTE Prototype V<sup>a</sup>**

Source/ Sending Compartment	Receiving Compartment	Moving Phase	Description of Advective Process	Units	Method for Calculation
Soil	Surface Water	Liquid	Runoff	m <sup>3</sup> (water)/day	= A*Runoff where: A = Area of soil layer, m <sup>2</sup> Runoff = Amount of runoff that reaches waterbody per unit area of watershed, m <sup>3</sup> (water)/m <sup>2</sup> (area)-day
Ground Water	Surface Water	Liquid	Recharge	m <sup>3</sup> (water)/day	=A*Recharge where: A = Area of soil-surface water interface, m <sup>2</sup> Recharge = Volume of water flow per unit area of interface, m <sup>3</sup> (water)/m <sup>2</sup> (area)-day
Air	Soil and Surface Water	Solid	Wet & Dry deposition of particles	m <sup>3</sup> (particles)/day	= A*v <sub>d</sub> * ρ <sub>A</sub> / ρ <sub>P</sub> where: A = Area of soil layer, m <sup>2</sup> v <sub>d</sub> = Dry deposition velocity of particles, m/day ρ <sub>A</sub> = Atmospheric dust load in air compartment type (concentration of dust in air), kg(particles)/m <sup>3</sup> (atmosphere) ρ <sub>P</sub> = Density of air particles, kg(particles)/m <sup>3</sup> (particles)
		Liquid	Wet deposition of liquid		Not implemented
	Air or Air Advection Sink	All phases	Wind advection	m <sup>3</sup> (air)/day	= A*u where: A = Area of air-air interface, m <sup>2</sup> u = Wind velocity from sending to receiving air compartment, m/day

**Table 2-1 (continued)**  
**Summary of Volumetric Advective Flow Velocities Included in TRIM.FaTE Prototype V<sup>a</sup>**

Source/ Sending Compartment	Receiving Compartment	Moving Phase	Description of Advective Process	Units	Method for Calculation
Air	Plant Leaf	Solid	Wet deposition of particles	m <sup>3</sup> (particles)/day	$= A * I * (w_d * \rho_A / \rho_P) * f_L$ where: A = Area of soil layer containing plant I = Interception fraction (see Chapter 7.0 for description of algorithm) v <sub>d</sub> = Deposition velocity of particles, m/day ρ <sub>A</sub> = Atmospheric dust load in air compartment type (concentration of dust in air), kg(particles)/m <sup>3</sup> (atmosphere) ρ <sub>P</sub> = Density of air particles, kg(particles)/m <sup>3</sup> (particles) f <sub>L</sub> = Fraction of deposition adhering that is taken up by plant
Surface Water	Sediment	Solid	Sediment deposition	m <sup>3</sup> (suspended sediment)/day	$= A * S_{dep} / \rho_{ss}$ where A = Area of surface water-sediment interface, m <sup>2</sup> S <sub>dep</sub> = Deposition rate of suspended sediment to sediment bed, kg(suspended sediment)/m <sup>2</sup> (area)-day ρ <sub>ss</sub> = Density of suspended sediment, kg(suspended sediment)/m <sup>3</sup> (suspended sediment)
	Surface Water	All phases	River flow	m <sup>3</sup> (air)/day	$= A * u_r$ where: A = Area of river parcel interface, m <sup>2</sup> u <sub>r</sub> = River velocity from sending to receiving river compartment, m/day

**Table 2-1 (continued)**  
**Summary of Volumetric Advective Flow Velocities Included in TRIM.FaTE Prototype V<sup>a</sup>**

Source/ Sending Compartment	Receiving Compartment	Moving Phase	Description of Advective Process	Units	Method for Calculation
Sediment	Surface Water	Solid	Sediment resuspension	m <sup>3</sup> (benthic sediment)/day	$= A \cdot S_{\text{resusp}} / \rho_{\text{bs}}$ where: $A$ = Area of sediment-surface water interface, m <sup>2</sup> $S_{\text{resusp}}$ = Resuspension rate of benthic sediment to water column, kg(benthic sediment)/m <sup>2</sup> (area)-day $\rho_{\text{bs}}$ = Density of benthic sediment, kg(benthic sediment)/m <sup>3</sup> (benthic sediment)
	Sediment burial sink	Solid	Sediment burial	m <sup>3</sup> (sediment)/day	Calculated so that amount of sediment buried is equal to maximum of 0 and amount deposited minus amount resuspended: $= A \cdot \max\{0, S_{\text{dep}}/\rho_{\text{ss}} - S_{\text{resusp}}/\rho_{\text{bs}}\}$ where: $A$ = Area of sediment-surface water interface, m <sup>2</sup> $S_{\text{dep}}$ = Deposition rate of suspended sediment to sediment bed, kg(suspended sediment)/m <sup>2</sup> (area)-day $\rho_{\text{ss}}$ = Density of suspended sediment, kg(suspended sediment)/m <sup>3</sup> (suspended sediment) $S_{\text{resusp}}$ = Resuspension rate of benthic sediment to water column, kg(benthic sediment)/m <sup>2</sup> (area)-day $\rho_{\text{bs}}$ = Density of benthic sediment, kg(benthic sediment)/m <sup>3</sup> (benthic sediment)

<sup>a</sup> Advection of chemicals to and from plants in particles and rain water and advection of chemicals to and from wildlife in dietary and excretory materials are not included. See Chapter 7.

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